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## (54) ACCELERATOR-CURED PHENOLIC RESIN GLUES

(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to compositions containing thermosetting alkaline phenol/formaldehyde condensates and curing accelerators.

Thermosetting phenol/formaldehyde condensates which have been precondensed under alkaline conditions (referred to below as phenolic resins) are extensively used as bonding agents in for example the wood-working industry and are used particularly extensively for making assemblies which are to be subjected to weathering.

It is common practice to use these phenolic resins in a water-soluble or water-dispersible state, the resulting wood glues thus being in the form of aqueous solutions or dispersions of said resins. The state of the resin at this stage is often referred to as the "resol" state. In this state, the phenolic resins substantially consist of low molecular weight methanol compounds of phenols in the form of their alkali metal salts.

For example, if it is desired to manufacture chipboard which is substantially water-proof, the appropriately prepared wood chips are sprayed with the (optionally diluted) aqueous solution or dispersion of the phenolic resin glue and then compressed with heating. The processes taking place in the binder phase of the wood/binder mixture are not known exactly, although certain fundamental processes taking place during the curing reaction, such as the elimination of water from methylol groups with mutual etherification, have been discerned. The dehydrated resins are initially still fusible, and this material is known to pass through a number of stages of different degrees of condensation, these being referred to as the "resol" state, the "resitol" state

and, finally, the "resite" state, in which the material is insoluble and infusible. There is usually no more free formaldehyde present in the resinous melt. The alkali present acts as curing catalyst.

It is known that the rate of the curing reaction may be accelerated by the presence of various materials. French Patent 1,550,846 discloses for example the use of inorganic and organic carbonates as curing accelerators.

Published German patent Application 1,469,823 proposes the use of formamide for the said purpose, and other materials such as lactones (see German Patent 1,065,605) have also been disclosed as curing accelerators.

All of these materials are effective as curing accelerators to a certain extent, although this does not mean that the action of these compounds is the same in each case. It is observed that the process of condensation, which, even at room temperature, slowly takes place in the aqueous solution of the resol, is accelerated by the addition of said compounds, as is manifest by an initial increase in the viscosity of the solution, after which the solubility limit of the resin is eventually overstepped and the solution gels or flocculates. This process is greatly accelerated at elevated temperatures. The gelling time, as measured at 100° C. for example, may be used as a measure of the curing rate afforded by the resinous composition when used in practice, for example as wood glue, although the actual course of the condensing process during hot-bonding of wood materials, which takes place in the substantial absence of water; does not quite correspond to the gelling process in aqueous solution.

It is obvious that catalytically active substances which are capable of accelerating a certain process at a certain elevated temperature are also catalytically active at lower temperatures. Thermosetting wood glues, which are usually used at temperatures of about 150° C., thus suffer a shortening of their pot-life when, as is usual, the curing accelerator is added thereto at room temperature. Whereas

thermosetting phenolic resin glues keep for a number of weeks, particularly when dilute, glues containing an accelerator begin to turn to gels after only a short period, with the result that their viscosity increases thus rendering the glues useless. This is particularly the case with those alkaline phenolic resin glues, which contain, as curing accelerator, cyclic carbonates or lactones.

The present invention therefore seeks to provide a curing accelerator for phenolic resin glues which has high accelerating activity at elevated temperature but does not shorten the pot-life of the glue unduly, especially to provide a wood glue which shows substantially constant viscosity over a relatively long period before use, which viscosity is relatively high at a moderate concentration of binder in the solution or dispersion of the glue resin. The higher the viscosity of the glue, without exceeding the solubility limit of the resin, the lower the tendency of the glue to penetrate the wood, thus losing its gluing properties.

We have now found that compositions containing thermosetting phenol/formaldehyde condensates which have been precondensed under alkaline conditions and which have a molar ratio of phenolic component, predominantly phenol, to formaldehyde of from 1:1.2 to 1:2.8 and which contain from 10 to 25% by weight of alkali metal hydroxide, based on the pure condensate, in aqueous solution or dispersion together with a curing accelerator, have a long pot-life and show high viscosity, whilst being capable of rapid curing at elevated temperatures, when the curing accelerator used is a mixture containing formamide as the major component and an amount of at least one compound selected from formates, carbonates, lactones, boric acid and alkali metal dichromates which is at least 1% of the weight of formamide but is insufficient to cause precipitation on addition to the composition.

A feature common to the compounds used together with the formamide is that they are known to be effective as curing accelerators when used alone but are difficult to use for this purpose on a commercial scale for certain reasons. Thus when a lactone, formate, carbonate, boric acid or an alkali metal dichromate is added to a phenolic resin solution, it is very difficult to prevent immediate formation of an insoluble precipitate at the point of initial addition, such a precipitate being difficult to redissolve. Such resin solutions prepared for accelerated curing by the addition of said compounds have only a relatively short pot-life and must often be used immediately after mixing. This is a serious drawback to commercial utilization of such curing accelerators. By blending such compounds with formamide, which, when used alone, suffers from the disadvantage that curing of the resin during pressing is too slow, there are obtained

mixtures which may be formulated to suit the various purposes in an excellent manner. The amount of such a compound that can be blended with formamide does not in general exceed 50% of the weight of formamide, if precipitation is to be avoided.

The water-soluble or water-dispersible, thermosetting phenol/formaldehyde condensates which have been precondensed under alkaline conditions are reaction products of a phenolic component, which is predominantly phenol, i.e. hydroxybenzene, although minor quantities of cresol, xylenol, resorcinol and similar phenols derived from benzene, alkylbenzenes and naphthalene can be used, with formaldehyde. These reaction products have a molar ratio of phenolic component to formaldehyde of from 1:1.2 to 1:2.8, preferably from 1:1.5 to 1:2.3, and contain from 10 to 25% by weight of alkali metal hydroxide, usually sodium hydroxide, and usually less than 1% by weight of free phenolic component and less than 2% by weight of free formaldehyde, based on the amount of resin. The aqueous resin solutions or dispersions normally have viscosities ranging from about 100 to 500 centipoise at a concentration of from 45 to 50% by weight of resin in the aqueous solution or dispersion. After the addition of the mixture of curing accelerators in accordance with the invention, the viscosity commonly reaches values of from 80 to 400 centipoise when the said mixture of curing accelerators is added in a concentration of from 2 to 8% by weight based on the aqueous condensate composition. It is observed, in practice, that the viscosity, for example at a concentration of 48% by weight of resin, rises from about 100 centipoise to about 250 centipoise (measured at 20° C.) during the pot-life of the mixture, which may be from 1 to 2 hours for example. Thus the phenolic resin compositions are usually diluted before use from their original concentration of say, 45—50% by weight to to a concentration of from 40—45% by weight. There is then added to the original or dilute solution or suspension usually from 2 to 8%, in particular from 4 to 6%, by weight of a mixture containing formamide and, per part by weight of formamide, from 0.01 to 0.5 part by weight and in particular from 0.02 to 0.3 part by weight of a lactone, a carbonate, formate, boric acid or an alkali metal dichromate.

Suitable formates are, for example, alkyl formates having from 1 to 5 carbon atoms in the alkyl radical, preferably 1 or 2 carbon atoms.

Suitable carbonates are, for example, those of aliphatic or cycloaliphatic alcohols such as dimethyl carbonate, diethyl carbonate, dicyclohexyl carbonate and, in particular, carbonates of aliphatic and cycloaliphatic glycols such as ethylene carbonate and propylene carbonate.

Very suitable curing accelerators are also blends containing lactones of hydroxycarboxylic acids of, say 4 to 12 carbon atoms, for example  $\gamma$ -butyrolactone and  $\alpha$ -hydroxyvalerolactone.

Of the above compounds, those preferred, mainly for economical reasons, are methyl formate, ethylene carbonate, propylene carbonate and  $\gamma$ -butyrolactone.

Other substances which, when mixed with formamide, have an accelerating action on curing, are boric acid and potassium or sodium dichromate.

Very good results are obtained when formamide is used with more than one of the said compounds as curing accelerator mixture. For example, it is particularly advantageous to use formamide with a combination of a lactone or a formate with boric acid or alkali metal dichromate. In such a case, it is convenient to use a mixture containing, per part of formamide, from 0.1 to 0.5 part by weight of a lactone or formate and from 0.01 to 0.2 part by weight of boric acid or alkali metal, dichromate. These blends are distinguished by the fact that they result in a very long pot-life of the mixed glue at room temperature but nevertheless cause rapid curing of the glue at moderately high working temperatures and provide, when the glue is used in the production of chipboard for example, hard wood materials showing a low degree of swelling.

It will be appreciated that compositions according to the invention may also be provided with dyes, insecticides, fungicides and other usual additives.

Chipboard may be manufactured, for example, by diluting commercially available ready-made phenolic resin glues to the desired consistency and adding the curing accelerator proposed in accordance with the invention

within a period of, say, from 1 to 2 hours before use. The glue may then be applied to loose wood chips in the usual manner by spraying, the binder being applied at a rate of, say, from 7 to 12% by weight based on the chip material. The sprayed material is laid out as a mat which is compressed in a press in which the plates have a temperature of, say, from 130° to 220° C. In the production of chipboard in the prior art it is necessary to use heating times of from 0.33 to 0.45 minutes per mm of board thickness. When the accelerator of the invention is added, the heating times found necessary have been from, say, 0.2 to 0.25 minutes per mm, which means, of course, that the production plant is utilized to a much better extent.

#### EXAMPLE 1.

A measure of the activity of a curing accelerator is the gelling time at 100° C. The test is carried out using an aqueous phenol/formaldehyde glue resin which has been prepared by condensing phenol with formaldehyde and caustic soda in a molar ratio of 1:2:0.75 at 98° C. in the usual manner and which has a viscosity of 145 centipoise at 20° C. and a solids content of 48%.

The gelling time at 100° C. is 60 minutes when no accelerator is added. The following Table shows that the addition of 6% of a curing agent mixture consisting of 25% of ethylene carbonate and 75% of formamide provides much shorter gelling times than those observed with mixtures of the same proportion of each component individually with water or with each component alone. Ethylene carbonate, when used alone, produces a precipitate immediately on addition to the phenolic resin, and this precipitate prevents uniform distribution of the binder on the material to be bonded.

Composition of curing mixture	Amount added	Gelling time at 100°C
25% ethylene carbonate	6%	5' 40"
75% formamide		
25% ethylene carbonate	6%	more than 20'
75% water		
25% water	6%	10' 20"
75% formamide		
100% formamide	6%	7' 45"
100% ethylene carbonate	6%	precipitation

The glue containing 6% of a mixture of 25% of ethylene carbonate and 75% of formamide as curing agent has a processing period of from about 2 to 3 hours, which is highly favorable for practical purposes.

#### EXAMPLE 2.

A curing solution is prepared by mixing 25 parts of 4-methyl-ethylene carbonate with 75 parts of formamide. The gelling time test is carried out using a phenolic resin which has been prepared in the usual manner by condensing phenol with formaldehyde and caustic soda in a molar ratio of 1:2:0.75. The resin solution has a viscosity of 152 centipoise at 20° C. and a solids content of 48%. The gelling time is about 60 minutes when no curing agent is added. The following gelling times at 100° C. are found when various proportions of curing mixture are added:

Amount of curing agent mixture added	Gelling time
4%	9' 10"
5%	7' 15"
6%	6' 25"
7%	5' 20"

The glue containing 6% of this curing mixture has an adequate pot-life of from 2 to 3 hours, whilst the addition of 6% of propylene carbonate to the phenolic resin renders the

glue unusable after only 10 minutes.

#### EXAMPLE 3.

A phenol/formaldehyde glue resin is prepared in the usual way using phenol, formaldehyde and caustic soda in a molar ratio of 1:2:0.75. The resin solution then has a viscosity of 150 centipoise at 20° C. and a solids content of 48% in aqueous solution.

A resin solution of the following composition is sprayed onto 4 kg of dried wood chips:

720 g of the above phenolic resin  
80 g of a paraffin emulsion (50% solid wax content)  
40 g of a mixture containing 75% of formamide and 25% of ethylene carbonate.

The treated chips are laid out in the form of a mat and then compressed at 165° C. under an applied pressure of about 25 kg/cm<sup>2</sup> to form a board. For the purposes of comparison, tests are carried out using no curing agent or using formamide alone as curing agent. The pressing time per mm of board thickness may be reduced by using the curing mixture of formamide and ethylene carbonate. Tests carried out on the boards as stipulated in German Standard Specifications DIN 52,360 to 52,365 give the results listed in Table 1 below. The corresponding ASTM standards are D 1037-64, sections 6 to 9, 27 to 32 and 69 to 75.

TABLE 1

Pressing Time in s/mm at 165°C	No curing agent		With 6% of formamide		With 6% of 75:25 mixture of formamide and ethylene carbonate	
	20	14.5	20	14.5	20	14.5
Thickness (mm)	18.5	No bonding occurs during this period and the resulting board is split	18.6	No bonding occurs during this period and the resulting board is split	18.6	18.6
Density (kg/m <sup>3</sup> )	680		678		681	678
Flexural Strength (kg/cm <sup>2</sup> )	311		306		312	310
Transverse tensile strength V 20 (kg/cm <sup>2</sup> )	6.8		7.2		7.8	7.9
V 100 (kg/cm <sup>2</sup> )	2.4		2.8		3.5	3.4
Percentage swell after 2 hours	6.3		5.5		4.8	5.0
24 hours	11.0		11.5		11.3	11.1

#### EXAMPLE 4.

2.1 kg of a phenolic resin prepared as described in Example 2 are mixed with 210 g of a 50% aqueous paraffin emulsion and 140 g of curing solution consisting of 95 parts of

formamide, 10 parts of 40% aqueous formaldehyde and 35 parts of propylene carbonate. This mixture is sprayed onto 10 kg of dry wood chips. The sprayed chips are then formed into a mat while still cold and are

subsequently compressed at a temperature of 165° C. The pressure applied during hot pressing is initially 22 kg/cm<sup>2</sup> and is reduced in steps during pressing until it is only 5 kg/cm<sup>2</sup>. The time required to compress the chipboard having a thickness of 20.6 mm is 4.5

minutes, i.e. 13.1 seconds per mm. Despite the extreme short pressing time, the resulting chipboard has the following data, as measured on 30 samples according to German Standard Specification DIN 68,761, Sheet 3:

Density strength	0.642 g/cm <sup>3</sup>
Flexural strength	289.7 kg/cm <sup>2</sup>
Transverse tensile strength after water immersion (24 h)	
at 20° C. (V 20)	5.7 kg/cm <sup>2</sup>
at 100° C. (V 100)	2.3 kg/cm <sup>2</sup>
Degree of swell after immersion in water for 24 hours at 20° C.	8.2%

#### EXAMPLE 5.

A measure of the activity of a curing accelerator is the gelling time of an accelerator-containing phenolic resin at 100° C. The test is carried out using an aqueous phenol/formaldehyde glue resin which has been prepared by condensing phenol with formaldehyde and caustic soda in a molar ratio of 1:2:0.75 at

98° C. in the usual manner and which has a viscosity of 162 centipoise at 20° C. and a solids content of 48%. The gelling time is 64 minutes at 100° C. when no curing agent is added. By adding various amounts of the curing mixtures listed in the following Table, the gelling times stated are obtained (at 100° C.):

Composition of curing mixture	4%	5%	6%	7%	8%
75:25 formamide/methyl formate	9' 04"	7' 37"	6' 07"	5' 27"	4' 25"
75:25 formamide/butyrolactone	10' 40"	7' 27"	6' 37"	5' 37"	5' 9"
80:20 formamide/butyrolactone	10' 33"	9' 22"	7' 25"	6' 13"	4' 41"

After the addition of 8% of formamide to the phenolic resin a gelling time of 7' 20" is measured. Neither the formate nor the lactone may be used alone as curing agent, since the viscosity of the glue rises too steeply after the addition.

#### EXAMPLE 6.

After the addition of 6% of a curing mixture consisting of 75% of formamide and 25% of methyl formate or 6% of a curing mixture consisting of 75% of formamide and 25% of butyrolactone to the glue described in Example 5, the pot-life at 25° C. is determined. The pot-life of the glues containing 6% of the formamide/methyl formate curing mixture or 6% of the formamide/butyrolactone mixture is from about 2 to 3 hours in each case, this being sufficient for practical purposes.

#### EXAMPLE 7.

2.08 kg of an aqueous phenolic resin prepared by condensing phenol, formaldehyde and caustic soda in a molar ratio of 1:2:0.75 are mixed with 200 g of a 50% aqueous paraffin emulsion and 130 g of a curing solution consisting of 78 parts of formamide and 52 parts of butyrolactone. This mixture is applied to 10 kg of dry wood chips by spraying. The coated chips are then compressed to chipboard

having a thickness of 20 mm by applying a pressure of 20 kg/cm<sup>2</sup> at 165° C. in the usual manner. The pressing time is 5 minutes, i.e. 15 seconds per mm. Tests on the resulting chipboard gave the following data:

Density	0.664 g/cm <sup>3</sup>
Flexural strength	302 kg/cm <sup>2</sup>
Transverse tensile strength	
V 20 (see Ex. 4)	7.0 kg/cm <sup>2</sup>
V 100 (see Ex. 4)	3.4 kg/cm <sup>2</sup>
Degree of swell after immersion in water for 24 hours at 20° C.	8.2%

In a comparative experiment in which the curing mixture of 52 parts of butyrolactone and 78 parts of formamide is replaced by 130 g of pure formamide as curing agent, parts of the chipboard expand when the pressure is removed, this indicating that formamide alone is not sufficient to cure the phenolic resin during the extremely short pressing time used.

#### EXAMPLE 8.

To 2.53 kg of an aqueous phenolic resin of the kind described above there are added 255 g of a 48% aqueous paraffin emulsion and 156 g of a curing solution consisting of 62 parts of butyrolactone, 85 parts of formamide

and 10 parts of 40% aqueous formaldehyde. The resulting mixture is sprayed onto 12 kg of dry wood chips and homogeneously distributed. The coated chips are precompressed in the cold to form a mat which is then compressed at a temperature of from 165° to 170° C. under a pressure of from 20 to 22 kg/cm<sup>2</sup> to form chipboard. The pressing time required for chipboard having a thickness of 20 mm is 5 minutes, i.e. 15 seconds per mm. The results of tests on the resulting chipboard carried out according to German Standard Specification DIN 68,761, Sheet 3, are as follows:

15	Density	0.625 g/cm <sup>3</sup>
	Flexural strength	298 kg/cm <sup>2</sup>
	Transverse tensile strength	
	V 20 (see Ex. 4)	6.9 kg/cm <sup>2</sup>
	V 100 (see Ex. 4)	3.43 kg/cm <sup>2</sup>
20	Degree of swell after immersion in water for 24 hours at 20° C.	8.1%

#### EXAMPLE 9.

2.06 kg of an aqueous phenolic resin of the kind described above are mixed with 218 g of a 50% aqueous paraffin emulsion and 152 g of a curing solution consisting of 120 parts of formamide and 32 parts of methyl formate. This glue composition is sprayed onto 9.8 kg of dry pine chips containing 30% of wood flour having an average particle size of less than 0.5 mm. The coated wood chips are

compressed at a temperature of from 165° to 170° C. under a pressure of 20 kg/cm<sup>2</sup> to form chipboard. The pressing time for chipboard of 20 mm in thickness is 4.5 minutes, i.e. 13.5 seconds per mm. Tests on the chipboard carried out according to DIN 68,761, Sheet 3, give the following results:

Density	0.666 g/cm <sup>3</sup>	
Flexural strength	295 kg/cm <sup>2</sup>	40
Transverse tensile strength		
V 20 (see Ex. 4)	5.9 kg/cm <sup>2</sup>	
V 100 (see Ex. 4)	2.8 kg/cm <sup>2</sup>	
Degree of swell after immersion in water for 24 hours at 20° C.	8.7%	45

#### EXAMPLE 10.

A measure of the activity of a curing accelerator is the gelling time of an accelerator-containing phenolic resin at 100° C. The test is carried out using an aqueous phenol/formaldehyde glue resin which has been prepared by condensing phenol with formaldehyde and caustic soda in a molar ratio of 1:2:0.75 at 98° C. in the usual manner and which has a viscosity of 165 centipoises at 20° C. and a solids content of 48%.

The gelling time at 100° C. is 68 minutes when no curing agent is included. By adding various amounts of the compounds or curing mixtures listed below, the following gelling times at 100° C. are obtained:

Compound or curing mixture	5%	6%	7%	8%
Potassium dichromate	sparingly soluble in the glue			
Boric acid	insoluble			
Methyl formate	precipitation occurs			
Butyrolactone	precipitation occurs			
Formamide	8' 40"	7' 50"	6' 50"	6' 0"
70:30 formamide/butyrolactone	8' 00"	—	5' 50"	5' 50"
70:30:2.5 formamide/butyrolactone/boric acid	7' 50"	6' 50"	5' 00"	4' 45"
70:30:10 formamide/butyrolactone/potassium dichromate	7' 50"	7' 00"	6' 25"	4' 20"
80:20:3 formamide/methyl formate/boric acid	7' 00"	6' 00"	5' 10"	4' 10"
80:20:15 formamide/methyl formate/potassium dichromate	6' 35"	6' 00"	6' 00"	4' 5"

As shown by the above data, the gelling time is 6 minutes after the addition of 8% of formamide to the phenolic resin. The curing mixtures of the invention, however, give gelling times between 4' 05" and 5' 50".

#### EXAMPLE 11.

2.16 kg of an aqueous phenolic resin of the composition described in the previous Example are mixed with 200 g of a 50% paraffin emulsion and 140 g of a curing solution consisting of 56 parts of butyrolactone, 74 parts of formamide, 8 parts of 40% formaldehyde and 3.5 parts of boric acid. This mixture of phenolic resin and curing solution is sprayed onto 9.96 kg of dry wood chips and homogeneously distributed. The resin-coated wood chips are then compressed to chipboard at temperatures of from 165° to 168° C. and under a pressure of 18 kg/cm<sup>2</sup>. The pressing time to obtain chipboard having a thickness of 16 mm is 3 minutes 40 seconds, i.e. 13.7 seconds/mm. Despite the very short pressing time, chipboard is obtained which complies with standard requirements in all respects. Tests carried out according to DIN 68,761, to Sheet 3, give the following results:

Density	0.675 g/cm <sup>3</sup>
Flexural strength	290 kg/cm <sup>2</sup>
Transverse tensile strength	
V 20 (see Ex. 4)	7.0 kg/cm <sup>2</sup>
V 100 (see Ex. 4)	3.0 kg/cm <sup>2</sup>
Degree of swell after immersion in water for 24 hours at 20°C.	9.3%

#### EXAMPLE 12.

To 2.11 kg of an aqueous phenolic resin of the composition described in Example 6 there are added 200 g of a 50% aqueous paraffin emulsion and 130 g of a curing solution consisting of 95 parts of formamide, 31.5 parts of methyl formate and 3.5 parts of boric acid. The resulting composition of phenolic resin, paraffin emulsion and curing solution is sprayed onto 10 kg of dry wood chips. The coated chips are then precompressed to a mat at room temperature and the resulting mat is soon afterward compressed to chipboard at temperatures between 160° and 170° C. and under a pressure of from 18 to 20 kg/cm<sup>2</sup>. The pressing time is 15 seconds/mm.

The chipboard so obtained has the following properties, as measured according to DIN 68,761, Sheet 3:

Density	0.628 g/cm <sup>3</sup>
Flexural strength	294 kg/cm <sup>2</sup>
Transverse tensile strength	
V 20 (see Ex. 4)	5.7 kg/cm <sup>2</sup>
V 100 (see Ex. 4)	2.44 kg/cm <sup>2</sup>
Degree of swell after immersion in water for 24 hours at 20°C.	8.3%

#### EXAMPLE 13.

Example 8 is repeated except that 154 g of a curing solution consisting of 56 parts of butyrolactone, 76 parts of formamide, 8 parts of 40% aqueous formaldehyde and 14 parts of potassium dichromate are used. Chipboard produced using this curing mixture has the following properties, as measured by DIN 68,761, Sheet 3:

Density	0.653 g/cm <sup>3</sup>
Flexural strength	280 kg/cm <sup>2</sup>
Transverse tensile strength	
V 20 (see Ex. 4)	7.37 kg/cm <sup>2</sup>
V 100 (see Ex. 4)	3.30 kg/cm <sup>2</sup>
Degree of swell after immersion in water for 24 hours at 20°C.	8.6%

#### EXAMPLE 14.

4.42 kg of a phenolic resin solution which has been prepared by condensing phenol with formaldehyde and caustic soda in a molar ratio of 1:2:0.75 are mixed with 900 g of water and 270 g of a solution of 95 parts of formamide and 5 parts of boric acid. This mixture is sprayed onto 27 kg of wood chips containing 2.2% of water and homogeneously distributed. The resin-coated chips are then compressed to chipboard at temperatures of from 165° to 168° C. and under a pressure of 18 kg/cm<sup>2</sup> using a pressing time of 13.5 s/mm. The resulting chipboard provides test results which comply with standard requirements according to DIN 68,761, Sheet 3, in all respects.

#### EXAMPLE 15.

665 parts of a phenolic resin of the kind described in the previous Example are mixed with 135 parts of water and 40 parts of a solution of 90 parts of formamide and 10 parts of potassium dichromate. This mixture is then sprayed onto 4,000 parts of bone-dry wood chips and homogeneously distributed. The coated wood chips are precompressed at room temperature to form a mat which is subsequently compressed to chipboard at temperatures of from 165° to 175° C. under a pressure of 20 kg/cm<sup>2</sup>. The pressing time used is 15 s/mm. The resulting chipboard shows good resistance to moisture and high mechanical strength properties, as measured by DIN 68,761, Sheet 3.

#### WHAT WE CLAIM IS:—

1. A composition containing a thermosetting phenol/formaldehyde condensate, which has been precondensed under alkaline conditions, and which has a molar ratio of phenolic component, predominantly phenol, to formaldehyde of from 1:1.2 to 1:2.8 and which contains from 10 to 25% by weight of alkali metal hydroxide, based on the pure condensate, in aqueous solution or dispersion

- together with a curing accelerator, wherein there is used as curing accelerator a mixture containing formamide as the major component and an amount of at least one compound selected from formates, carbonates, lactones, boric acid and alkali metal dichromates which is at least 1% of the weight of formamide but is insufficient to cause precipitation on addition to the composition.
2. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 wherein the total amount of formates, carbonates, lactones, boric acid and alkali metal dichromates in the curing accelerator does not exceed 50% of the weight of formamide.
3. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 or 2, wherein the curing accelerator is a mixture comprising formamide and an alkyl formate having 1 to 5 carbon atoms in the alkyl radical.
4. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 or 2 wherein the curing accelerator is a mixture comprising formamide and a lactone of a hydroxycarboxylic acid having 4 to 12 carbon atoms.
5. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 or 2 wherein the curing accelerator is a mixture comprising formamide and a carbonate of an aliphatic or cycloaliphatic glycol.
6. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 or in claim 3 or 4 as appendent to claim 1, containing, as curing accelerator, from 2 to 8 percent by weight, based on the composition of a mixture of formamide and, based on the formamide, from 10 to 50 percent by weight of a lactone or formate and from 1 to 20 percent by weight of boric acid or an alkali metal dichromate.
7. A thermosetting phenol/formaldehyde condensate composition as claimed in claim 1 and substantially as hereinbefore described and exemplified.
8. A method of bonding wood comprising applying a thermosetting phenol/formaldehyde condensate composition as claimed in any of claims 1 to 7 to wood.
9. A process of producing chipboard comprising applying a thermosetting phenol/formaldehyde condensate composition as claimed in any of claims 1 to 7 to loose wood chips.
10. A process of producing chipboard as claimed in claim 9 substantially as described with reference to any of the foregoing Examples.
11. Chipboard when produced by a process as claimed in claim 9 or 10.
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